

**Title:** HYDROGEN SEPARATION THROUGH PORE SIZE ENGINEERED ZEOLITE MEMBRANES

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## 1. ABSTRACT

### Objective

Zeolites are microporous crystalline aluminosilicates, having cage-like structures of precise geometry with pores of uniform shape. Zeolites can act as molecular sieves and can be used for separating gas mixtures. Zeolite membranes can withstand wide temperature and pressure ranges and chemically challenging environment, thus can be used in catalytic membrane reactor applications related to coal conversion and gasification. The pore sizes of different zeolite types are discontinuous however; and to date zeolite membranes have not been made very successful for hydrogen separation from other light gases. So the pore size of currently used zeolite membranes need to be engineered in order to alter the molecular sieving and adsorption selectivity in a controlled way.

### Accomplishments to Date

To effectively engineer the pore size of zeolite membranes for hydrogen separation, silylation reactions have been used with proper silane precursors. In this reaction, the silane compound was firstly chemisorbed onto the acid sites within the zeolite membrane, then catalytically cracked on sites and oxidized. As a result, additional silicon atoms were added to the original zeolite structures, and the effective pore opening size was modified. Another approach to engineer the pore size of zeolite membranes, which is exchanging the existing ions in the zeolite structure with different metal ions or protons, has also been tried. The exchange is tunable by the proper choice of ions.

Two different types of zeolite membranes have been silylated: medium pore MFI membranes with ten-membered ring structure and small pore SAPO-34 membranes with eight-membered ring structure. The silylation reaction could reproducibly improve the hydrogen separation performance for both types of zeolite membranes.

For MFI type zeolite membranes, the silane precursor compound could penetrate into the medium-sized zeolite pores. Thus after silylation, the zeolite pores were partially blocked. As a result, hydrogen selectivity over other light gases

(CO<sub>2</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>) all increased. Gas permeation rate did not follow the order of kinetic diameter, and CO<sub>2</sub> became the slowest permeating molecule. The H<sub>2</sub>/CO<sub>2</sub> ideal selectivity can be as high as 235 for the silylated MFI membranes, as compared with only 1.8 for the original membrane. The H<sub>2</sub> permeance however, decreased more than an order of magnitude. For H<sub>2</sub>/CO<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub> binary mixture separations, the modified MFI membrane was selective towards H<sub>2</sub> in the entire temperature range explored. And the membrane became more promising at higher temperatures, as the H<sub>2</sub> permeance as well as separation selectivity increased with increasing temperatures.

For SAPO-34 membranes, the silane precursor compound did not penetrate into the zeolite pores due to the small pore size. So only the pore entrance area and the bigger non-zeolite defects were affected. As a result, hydrogen permeance was almost unchanged after silylation. The silylation reaction increased the membrane H<sub>2</sub>/CH<sub>4</sub> separation performance, and separation selectivity can be increased more than 50% from 35 to 59. The H<sub>2</sub>/CO<sub>2</sub> separation selectivity, however, did not change much. The silylation reaction is also effective in improving CO<sub>2</sub>/CH<sub>4</sub> separation performance of the SAPO-34 membrane. The CO<sub>2</sub>/CH<sub>4</sub> separation selectivity could be improved from 73 to 110, with the CO<sub>2</sub> permeance deduction of about 20%.

Liquid state ion exchange on SAPO-34 membranes has been started. The initial result of Cu(II) ion exchanged SAPO-34 membrane showed increased H<sub>2</sub> permeance and H<sub>2</sub>/CH<sub>4</sub> selectivity. The Cu(II) ion exchange also improved the membrane CO<sub>2</sub>/CH<sub>4</sub> separation selectivity from 49 to 69, with the CO<sub>2</sub> permeance deduction of only 10%.

### **Future Work**

- Continue the ion exchange on SAPO-34 membranes with different ions, for example potassium and cerium.
- Obtain gas adsorption isotherms and the chemical structures of zeolite powders before and after modification in order to understand the underlying factors that cause gas transport changes.
- Find high temperature and high pressure sealing technique for tubular zeolite membranes and study the hydrogen separation performance at higher temperatures and pressures.
- Organize and publish the outcome of these investigations
- Try synthesizing 6-member ring zeolite membranes. Six-membered ring zeolite membranes have rarely been reported in the literature. Membrane synthesis methods will be developed by modifying the procedures for making their powders.

## **2. LIST OF PAPER PUBLISHED, U.S. PATENT/PATENT APPLICATION(S), CONFERENCE PRESENTATIONS, STUDENTS SUPPORTED UNDER THIS GRANT**

### **Conference Presentations**

Light gas separations through silylated zeolite membranes, M. Hong, R.D. Noble, J.L. Falconer, 3<sup>rd</sup> international zeolite membrane meeting, 2004, submitted.

### **Students Supported Under this Grant**

Mei Hong, graduate student in the Department of Chemical and Biological Engineering, University of Colorado.